

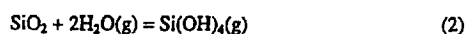
THE PARALINEAR OXIDATION OF SiC IN COMBUSTION ENVIRONMENTS

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SiC is proposed for structural applications in high pressure, high temperature, high gas velocity environments of turbine and rocket engines. These environments are typically composed of complex gas mixtures containing carbon dioxide, oxygen, water vapor, and nitrogen. It is known that the primary oxidant for SiC in these environments is water vapor [1]. The oxidation reaction occurs by the reaction:



In addition, it has been found that the SiO_2 forms a volatile hydroxide in these environments by the following reaction [2-5]:



The oxidation/volatilization reactions follow parabolic kinetics [6]. These kinetics have been modeled by Tedmon [7] for chromia forming alloys and are directly applicable to SiC oxidation/volatilization:

$$dx/dt = k_p/2x - k_l \quad (3)$$

where x is the oxide thickness, t is the time, k_p is the parabolic oxidation rate constant, and k_l is the linear volatilization rate constant. At long times a steady state is achieved in which the oxide growth rate becomes equal to the oxide volatilization rate. Under these conditions a constant oxide thickness, x_{limit} , is found that is given by:

$$x_{\text{limit}} = k_p/2k_l \quad (4)$$

The parabolic oxidation rate constant, k_p , has been studied as a function of water vapor partial pressure and temperature [8,9]. These dependencies have been summarized in Table 1.

The pressure, temperature, and gas velocity dependence of the linear volatilization rate constant, k_l , have been measured empirically [4]. They have also been modeled using an expression for gas boundary layer transport [5]:

$$k_l = 0.664 (Lv\rho/\eta)^{1/2} (\eta\rho/D)^{1/3} D\rho/L \quad (5)$$

where v is the gas velocity, η is the gas viscosity, D is the interdiffusion coefficient of $\text{Si}(\text{OH})_4$ in the combustion gas boundary layer, ρ is the concentration of $\text{Si}(\text{OH})_4$ at the silica/gas interface, and L is a characteristic length. This expression for k_l can be reduced to the combustion variables of pressure and velocity:

$$k_l \propto v^{1/2} P_{\text{total}}^{3/2} \quad (6)$$

Remarkable agreement between the empirical and boundary layer transport model was found [4,5].

The pressure, temperature, and gas velocity dependencies for the rate constants k_p and k_l are summarized in Table 1. Because of these different dependencies, the limiting oxide thickness (Eq. 4) under different combustion conditions varies. The variation in this thickness has been explored with respect to the rate constants as well as the pressure, velocity, and temperature and is shown in oxide thickness maps in Figures 1 and 2. Examples of predicted limiting oxide thickness are shown for various conditions.

References

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Table 1. Pressure, temperature, and velocity dependence for oxidation and volatilization rate constants.

n, P(H ₂ O) ⁿ	T dependence (kJ/mol)	m, v ^m	Comments, reference
Parabolic oxidation rate, k_p			
0.67±0.19	28 to 156	n/a	[8]
0.85±0.05		n/a	Si, [10]
1.0	68	n/a	[9]
0.91±0.10	—	n/a	[9]
Linear volatilization rate, k_l			
1.50±0.13	108±7	0.50±0.16	[4]
1.5	—	0.50	calculated, [5]
—	56.7±1.7	—	[2]
—	3±75	—	[8]

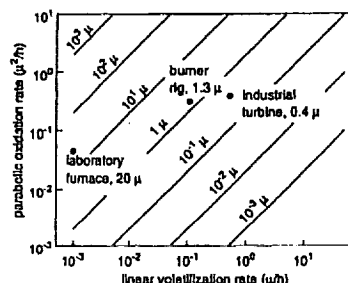


Figure 1. Limiting oxide thickness map as a function of oxidation and volatilization rate constants.

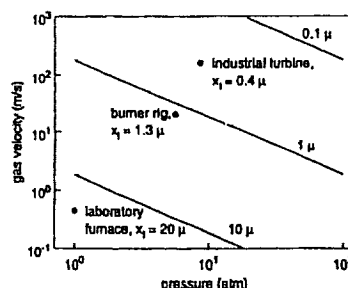


Figure 2. Limiting oxide thickness map as a function of pressure and gas velocity in the combustion environment at 1300°C.